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## **Photoluminescence of ZnBeMnSe solid solutions**

**K. Strzałkowski, F. Firszt, A. Marasek**

Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziadzka 5, 87-100 Torun, Poland

Corresponding author: K. Strzałkowski, skaroll@fizyka.umk.pl, +48692631318

### **Abstract**

In this paper optical properties of  $\text{Zn}_{1-x-y}\text{Be}_x\text{Mn}_y\text{Se}$  mixed semiconductors were studied as a function of both, temperature and excitation power. The crystals under investigation were grown by the high-pressure, high-temperature vertical Bridgman technique within the range of the composition  $0.05 \leq x, y \leq 0.2$ . Photoluminescence spectra for the lowest content of Mn and Be exhibit character typical for II-VI semiconductors together with intensive yellow-orange manganese emission. Evolution of the excitonic emission as the function of temperature allowed determining the energy gap of the investigated semiconductors. Absorbance and photoluminescence excitation spectra confirmed crystal field splitting of excited atomic terms of manganese ions into the states, denoted according to the crystal field theory in the case of tetrahedral symmetry. Temperature and laser power dependences of luminescence showed anomalous behavior of the manganese emission. It turned out that the position of the  $\text{Mn}^{2+}$  related luminescence band does not change monotonically with the variation of the temperature or the excitation power. Finally, switching of the manganese emission has been observed. By increasing laser power of exciting radiation, the Mn-related emission could be quenched by almost two orders in magnitude. This effect was especially strong at low temperature and it was fully reversible.

**Keywords:** II-VI crystals; ZnBeMnSe mixed semiconductors; Photoluminescence; Manganese emission; Crystal field theory

## 1 Introduction

II-VI semiconductors are promising materials for application in construction of visible radiation sources, green laser diodes, in spintronics, photodetection and other branches of modern optoelectronics [1]. From the application point of view, the main feature of the ternary and quaternary II-VI compounds is the possibility of smooth change of the band gap energy and lattice constant values by variation of composition [2]. The beryllium in II-VI ternary and quaternary compounds plays also a significant role because of hardening and stabilizing the crystal structure [3]. Diluted Magnetic Semiconductors based on II-VI mixed crystals with manganese as constituent, such as  $\text{Zn}_{1-x-y}\text{Be}_x\text{Mn}_y\text{Se}$  are very promising materials for spintronics due to their unique magnetic and optical properties [4]. Magnetic and magnetooptical properties of manganese containing II-VI solid solutions arise from the interaction between charge carriers and the magnetic  $\text{Mn}^{2+}$  ions placed in the cation site [5-7]. Apart from magnetic properties, this compound exhibits very interesting optical properties and can serve as luminescence material [8]. Crystal field of tetrahedral symmetry splits degenerated atomic terms of the manganese ions incorporated into the lattice [9]. Thanks to that one can observe absorption bands connected with the transitions from ground state to next excited states of Mn ion. The number of states visible in the absorption spectrum depends on the energy gap of the host crystal. Once the sample is excited, the intensive yellow-orange emission takes place, easily visible by eye even at room temperature. Due to the possible application as a component of phosphors, the  $\text{Mn}^{2+}$  emission was intensively studied for more than sixty years. Nowadays the topic is still under investigation, especially in the field of nanotechnology [10-12].

This work is some kind of review summarizing optical properties of  $\text{Zn}_{1-x-y}\text{Be}_x\text{Mn}_y\text{Se}$  crystals grown by our group. Composition, temperature and finally laser power dependent PL spectra were measured. The aim of the paper is to analyze and discuss the mentioned above dependencies. Among expected and known phenomena some new results were obtained. The temperature evolution of the manganese emission showed anomalous behavior. Some unexpected results were obtained also for laser power dependent spectra. Systematic investigations revealed a completely new effect. For the samples with high manganese content at low temperatures and for some laser powers optical switching of the manganese emission has been observed. The intensive yellow-orange manganese emission could be quenched by increasing of excitation laser power almost two orders in magnitude. After decreasing laser power to previous level the luminescence was restored.

## 2 Material and methods

The crystals under investigation were grown from the melt by the high-pressure (150 atm of argon) modified Bridgman method using high purity powders of ZnSe (99.9999%), Be (99.8%), Mn (99.95%) and Se (99.999%) put in a graphite crucible. The  $\text{Zn}_{1-x-y}\text{Be}_x\text{Mn}_y\text{Se}$  solid solutions were obtained in the range of composition  $0.05 < x, y < 0.2$ .

Grown crystal rods (1 cm in diameter) were cut into about 1.5 mm thick plates. The samples were first ground using the grinding powder ( $\text{Al}_2\text{O}_3$ , 10  $\mu\text{m}$  in diameter) and next polished with the diamond paste (1  $\mu\text{m}$ ) until receiving a mirror-like surface. After polishing samples were chemically etched in solution of sulfuric acid (96%), potassium dichromate and water. The transmission spectra were measured using polished samples, but photoluminescence

measurements were carried out after chemical etching. More details concerning growing procedure and samples surface treatment can be found elsewhere [13,14].

For checking real Zn and Mn contents the SEM/EDS analysis was applied. The Be content was calculated assuming that the sum of cation (Zn, Mn, Be) contents (in at.%) is equal to that of Se anion. This technique gives results with the accuracy of about 0.005 for the investigated in this work range of the composition.

Two standard photoluminescence setups were applied. The first one consisted of He-Cd laser (325 nm, 20 mW), xenon lamp (Cemax), SPM-2 (Carl-Zeiss-Jena) monochromator, photomultiplier (Hamamatsu), cryostat and temperature controller. This setup was used for temperature dependent photoluminescence and excitation spectra measurement in the range of 30 K to RT. Spectral resolution of such system depends mainly on entrance slit width. Here typical value was of the order of 0.05 nm up to 0.3 nm, depending on the intensity of the upcoming radiation. These values correspond to the spectral resolution of 0.2 nm and 1.2 nm for 400 nm and 700 nm spectral regions respectively. The measurements were performed with the step of 1 nm.

Some results were also obtained applying a new setup, which consisted of lasers (He-Cd and 405 nm diode laser with output power up to 300 mW), helium cryostat (Advanced Research Systems), temperature controller (LakeShore 331) and the spectrometer (MicroHR Horiba Jobin Yvon) equipped with diffraction gratings (1200 lines/mm or 2400 lines/mm), filter wheel and thermoelectrically cooled CCD camera (Synapse Horiba Jobin Yvon, 1024x256 pixels). All measurements were performed in the temperature range from 10 K to RT. In this case spectral resolution was about 1 nm. The transmission and excitation spectra at RT were measured using Perkin-Elmer spectrometer (model Lambda Series/PECSS) and Perkin-Elmer LS-50B, respectively. The dynamics of used spectrophotometer was about 3 in the case of absorbance what means that such system can measure the intensity of transmitted radiation through the sample within three orders in magnitude.

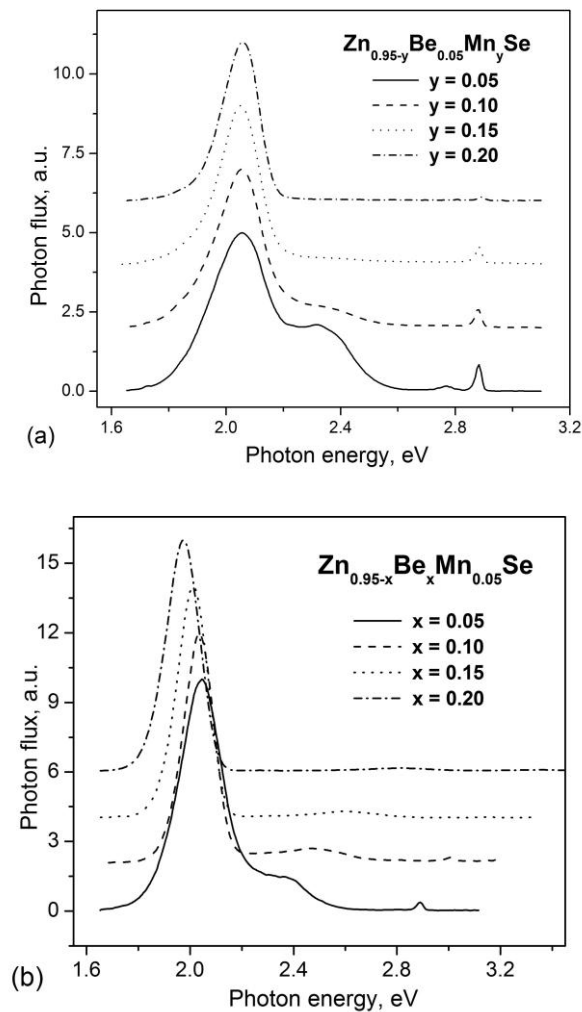
### 3 Results and discussion

#### 3.1 General photoluminescence properties

A typical photoluminescence spectrum of wide-gap II-VI semiconductor consists of exciton emission, so called edge luminescence with visible (or not) phonon structure and wide bands connected with presence of deep levels. In the case of manganese doped ZnSe or ZnS crystals additional and dominant component of the whole spectrum is intensive yellow-orange emission. The origin of this luminescence is the radiative interband recombination which takes place only inside  $\text{Mn}^{2+}$  ions within d-shell between first excited and ground states [9]. This is in the contrary to other intraband recombination processes occurring within energy levels of the crystal. It is well established now that the ground state of manganese ion corresponds to the situation when all five d-electrons have the same spin orientation. According to the crystal field theory this state is denoted as  ${}^6\text{A}_1({}^6\text{S})$ . The reversal of the spin of the subsequent electrons produces excited states with increased energy.

Fig. 1 presents the photoluminescence spectra of  $\text{Zn}_{1-x-y}\text{Be}_x\text{Mn}_y\text{Se}$  crystals measured at 30 K under 325 nm excitation as a function of manganese (a) and beryllium (b) content. The spectrum of  $\text{Zn}_{0.9}\text{Be}_{0.05}\text{Mn}_{0.05}\text{Se}$  sample (solid line in picture (a)) consist of excitonic line positioned at 2.88 eV, weak edge emission with the maximum at 2.77 eV, green band at 2.35

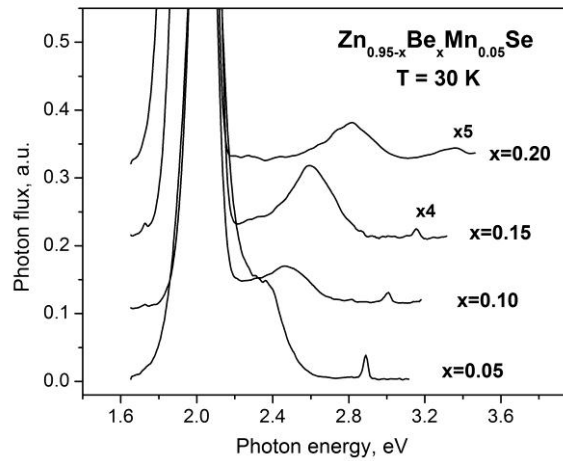
eV and intensive yellow-orange photoluminescence with the position at 2.05 eV. One can see that obtained spectra follow more or less description of presented above, characteristic emission of II-VI crystals, however there are significant differences which must be pointed out. Phonon replicas in the edge emission are not visible and full width at half maximum of exciton emission is of the order of 25 meV (much larger than in binary ZnSe). Those are typical phenomena for mixed ternary and quaternary compounds and are connected with lattice disorder effects. It was also observed that with increasing of Be content the intensity of the exciton emission line noticeably decreases comparing to the yellow emission (Fig. 1b and Fig. 2). For samples with beryllium content larger than 0.05 the exciton line is very weak at low temperatures but at room temperature only yellow PL band is observed. This is in agreement with the observations for  $\text{Zn}_{1-x}\text{Be}_x\text{Se}$  crystals grown by the same method [15] where the intensity of exciton emission decreased with increasing of Be content.



**Fig. 1** Photoluminescence spectra of investigated  $\text{Zn}_{1-x-y}\text{Be}_x\text{Mn}_y\text{Se}$  crystals measured at 30 K for different content of manganese (a) and beryllium (b).

It was also observed (see Fig. 1b), that in  $\text{Zn}_{0.95-x}\text{Be}_x\text{Mn}_{0.05}\text{Se}$  samples with constant concentration of Mn the main Mn-related yellow emission band shifts towards lower photon energies with increasing of beryllium content. The measured lattice constant of investigated crystals showed that with increasing of Be content the lattice constant decreases.

On the other hand, in case of  $\text{Zn}_{0.95-y}\text{Be}_{0.05}\text{Mn}_y\text{Se}$  alloys, where the Mn content increases from 0.05 up to 0.2 one can see the  $\text{Mn}^{2+}$  luminescence does not change its energetic position. The same observation can be done for excitonic emission. The conclusion is that the crystal field and the energy gap do not vary noticeably with the increasing Mn content in the investigated range of composition. Indeed, it was observed that the energy gap of  $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$  crystals do not change much in the given range of Mn concentration [16]. On the other hand, in case of increasing beryllium content (Fig. 1b and Fig. 2) it is clearly seen that both, exciton and manganese luminescence shift with increasing of Be content. The excitonic line shifts towards higher energy and follows increasing energy gap of the compound. Similar high-energy shift is observed for the “green” emission band. The yellow PL band exhibits redshift.



**Fig. 2** Near band-edge PL spectra at 30 K of four  $\text{Zn}_{0.95-x}\text{Be}_x\text{Mn}_{0.05}\text{Se}$  crystals with varying Be content.

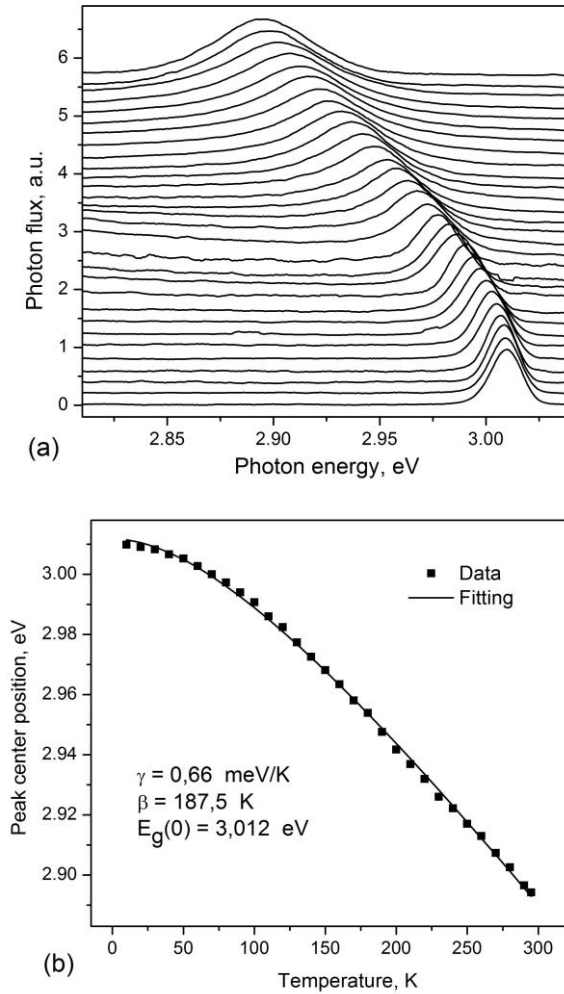
It was shown previously [17], that adding beryllium to the structure increases significantly the energy gap of the crystal. At the same time the character of the bonding changes from the ionic to more covalent one and as a consequence the lattice constant decreases. This is because of unusual in case of II-VI semiconductors pure BeSe properties. Binary beryllium selenide does not exist in nature, however theoretical calculations predict covalent character of the Be-Se bonding, energy gap of the order of 5 eV and small lattice constant. The crystal field splitting atomic terms of manganese ion increases as the lattice shrinks, consequently the ground  ${}^6\text{A}_1({}^6\text{S})$  and first excited states approach to each other and the energy of the emissions is getting lower. Therefore basic optical characterization of the given semiconductors is of high importance.

The excitonic energy position (which follows energy gap) of the investigated crystals has been determined from the temperature evolution of the exciton luminescence. It is known that in the case of direct semiconductor the temperature dependence of the energy gap can be described by Varshni formula:

$$E_g(T) = E_g(0) - \frac{\gamma \cdot T^2}{\beta + T} \quad (1)$$

where  $E_g(0)$  is the value of the band gap at temperature 0 K. Constants  $\gamma$  and  $\beta$  are connected with electron (exciton) – phonon interaction and Debye temperature, respectively. The temperature evolution of energetic position of exciton line in  $\text{Zn}_{0.85}\text{Be}_{0.1}\text{Mn}_{0.05}\text{Se}$  crystal from 10 K to RT and fitting of the Varshni formula to the experimental data are presented in Fig. 3a

and Fig. 3b, respectively. The observed emission shifts monotonically with the temperature increasing towards lower energies, simultaneously thermal broadening takes place. This is normal and expected behavior of the free exciton recombination. In such a case the position of the line corresponds directly to the energy gap value with an accuracy of exciton binding energy. The excitonic origin of the emission line corresponding to the highest energy in emission spectrum at low temperatures has been confirmed by reflectivity measurements. At high temperatures the excitons have significant kinetic energy and, because of momentum conservation, the radiative recombination or free excitons must be accompanied by some interactions with phonons or carriers. The most probable mechanism of this emission at high temperatures is the free exciton recombination after their interaction with free carriers.



**Fig. 3** Temperature exciton evolution for  $\text{Zn}_{0.85}\text{Be}_{0.1}\text{Mn}_{0.05}\text{Se}$  sample (a) and fitting of Varshni formula to the experimental data (b) from 10 K to 300 K.

The energetic position of the exciton emission lines on the composition for all investigated crystals are presented in Table 1. Only a very small increase in  $E_g$  value with increasing Mn content can be seen for  $\text{Zn}_{0.95-y}\text{Be}_{0.05}\text{Mn}_y\text{Se}$  crystals. On the contrary, the energy gap varies from 2.799 eV to 3.26 at room temperature when the beryllium content increase from 0.0 to 0.2. Both cases confirm our earlier observations. Taking into account the accuracy of determining the position of the exciton line one can estimate its uncertainty as 5-10 meV.

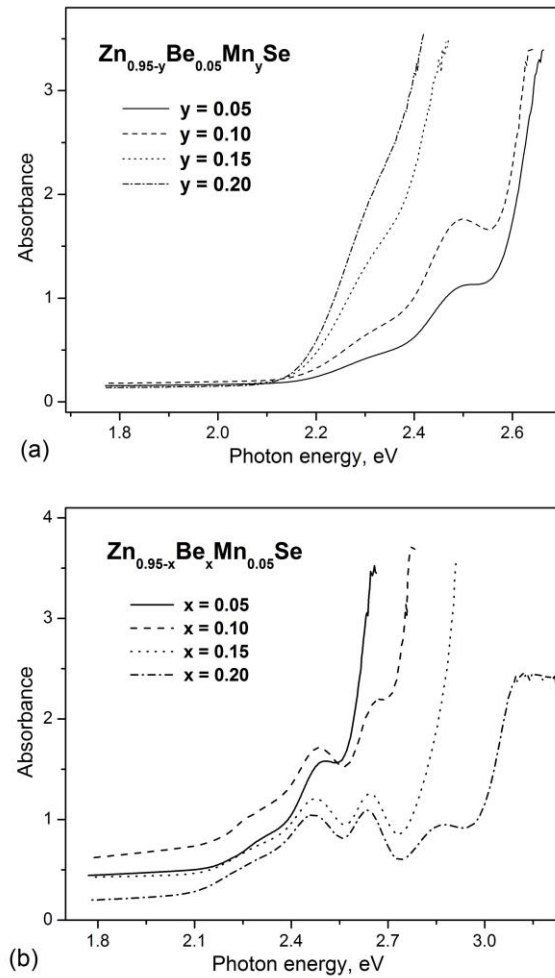
Since exciton binding energy in the case of typical II-VI crystal like ZnSe is of the order of 20 meV one should keep in mind that the real  $E_g$  value is slightly higher.

**Table 1** The composition dependence of the energy of exciton emission in  $\text{Zn}_{1-x-y}\text{Be}_x\text{Mn}_y\text{Se}$  crystals.

$x$	0.05	0.05	0.05	0.05	0.05	0.1	0.15	0.2
$y$	0.05	0.1	0.15	0.2	0.05	0.05	0.05	0.05
$E_g$ at 30 K	2.911	2.912	2.913	2.92	2.923	3.011	3.181	3.384
$E_g$ at 300 K	2.787	2.788	2.789	2.796	2.799	2.908	3.057	3.26

### 3.2 Absorbance and photoluminescence excitation spectra

Fig. 4 presents absorbance spectra of investigated  $\text{Zn}_{1-x-y}\text{Be}_x\text{Mn}_y\text{Se}$  crystals measured at RT for varying Mn (a) and Be (b) content.

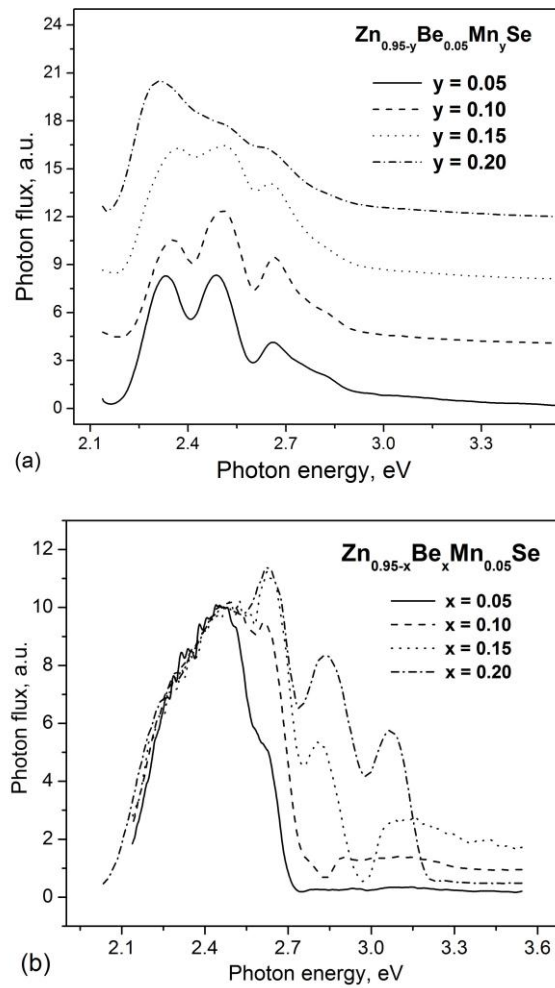


**Fig. 4** Absorbance spectra of  $\text{Zn}_{1-x-y}\text{Be}_x\text{Mn}_y\text{Se}$  crystals measured at RT for varying Mn (a) and Be (b) content.

On the picture (a) characteristic Mn-related absorption bands can be seen, however the structure vanishes for higher Mn concentration. There are two explanations for this fact: (i) higher content of  $\text{Mn}^{2+}$  ions corresponds directly to higher absorption coefficient and wider bands and (ii) the dynamics of used spectrophotometer was only 3 in absorbance and the

thickness of the sample was of the order of 1 mm. As the consequence the bands overlap each other and some saturating effects takes place.

On the other hand in case of absorbance spectra of  $\text{Zn}_{0.95-x}\text{Be}_x\text{Mn}_{0.05}\text{Se}$  mixed crystals presented in Fig. 4b for highest beryllium content one can see well resolved absorption bands up to 3 eV. The excited energy levels of  $\text{Mn}^{2+}$  ion progressively reveal as the energy gap increases with increasing Be concentration. According to the crystal field theory, the observed absorption bands are connected with spin flipping of the d-shell electrons. Since II-VI crystals exhibits tetrahedral symmetry the crystal fields splits degenerated atomic terms into following excited states:  ${}^4\text{T}_1({}^4\text{G})$ ,  ${}^4\text{T}_2({}^4\text{G})$ ,  $({}^4\text{A}_1, {}^4\text{E})({}^4\text{G})$ ,  ${}^4\text{T}_1({}^4\text{P})$  and  ${}^4\text{E}({}^4\text{D})$  [18]. However, according to Ford [19], the fourth state is  ${}^4\text{T}_2({}^4\text{D})$  instead of  ${}^4\text{T}_1({}^4\text{P})$ . The spectrum in picture (b) for  $\text{Zn}_{0.75}\text{Be}_{0.2}\text{Mn}_{0.05}\text{Se}$  crystal consists of five clearly resolved components at energies equal to 2.30 eV, 2.48 eV, 2.64 eV, 2.86 eV and 3.08 eV.



**Fig. 5** Photoluminescence excitation spectra of Mn-related PL in  $\text{Zn}_{1-x-y}\text{Be}_x\text{Mn}_y\text{Se}$  solid solutions measured for different composition of Mn and Be at 30 K (a) and RT (b), respectively.

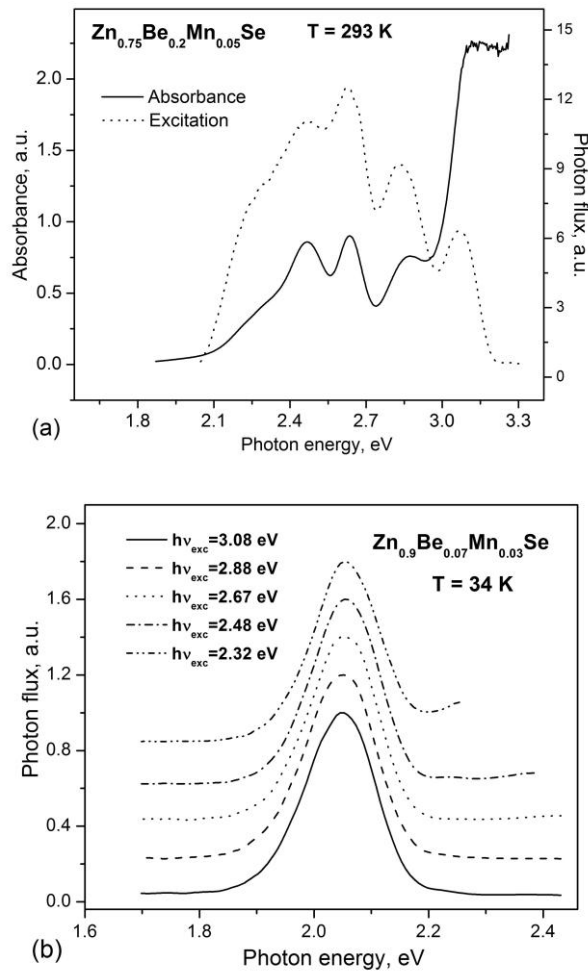
These values are close to energies in absorption spectrum of  $\text{ZnS}:\text{Mn}$  cubic single crystals observed by McClure [20] and Ryskin *et al* [21] and can be interpreted as associated with transitions from the ground  ${}^6\text{A}_1({}^6\text{S})$  state of  $\text{Mn}^{2+}$  to different excited states.



The number of visible components in absorption spectrum is limited by the value of the energy gap since for  $\text{Zn}_{1-x-y}\text{Be}_x\text{Mn}_y\text{Se}$  with low Be content higher excited levels of Mn are located within conduction band. For  $\text{Zn}_{0.95-y}\text{Be}_{0.05}\text{Mn}_y\text{Se}$  alloys at RT only two transitions are visible. With increasing of Be content transitions associated with higher excited states of Mn clearly appear in the absorption spectra due to increasing of the energy gap.

The photoluminescence-excitation (PLE) spectra when the emission is detected at the maximum of the yellow Mn emission, exhibit structure which is related to the internal transitions in Mn ion. Fig. 5a and b present the PLE spectra when the emission is detected at 2.0 eV (maximum of the yellow Mn emission) of  $\text{Zn}_{1-x-y}\text{Be}_x\text{Mn}_y\text{Se}$  solid solutions for different composition of Mn and Be measured at 30 K (a) and RT (b), respectively.

The spectra measured at  $T=30$  K of  $\text{Zn}_{0.95-y}\text{Be}_{0.05}\text{Mn}_y\text{Se}$  samples consist of four clearly resolved components at the energies 2.30 eV, 2.48 eV, 2.68 eV and 2.85 eV. The lower Mn content in the crystal the better resolved the structure is. One can also distinguish a fifth maximum positioned at the energy about 3.1 eV.



**Fig. 6** Comparison of photoluminescence excitation and absorbance spectra of  $\text{Zn}_{0.75}\text{Be}_{0.2}\text{Mn}_{0.05}\text{Se}$  crystal (a) and Mn-related emission of  $\text{Zn}_{0.9}\text{Mn}_{0.03}\text{Be}_{0.07}\text{Se}$  sample measured under different energies of exciting radiation (as indicated on the figure) corresponding to maxima on the PLE spectrum.

These values are very close to energies in absorption spectrum of  $\text{ZnS:Mn}$  cubic single crystals observed by McClure [20] and Ryskin *et al* [21] and rather well correspond to

maxima in the absorption spectra presented in Fig. 4 (see also comparison in Fig. 6a). Similar results were obtained by Oczkiewicz *et al* for  $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$  system [22].

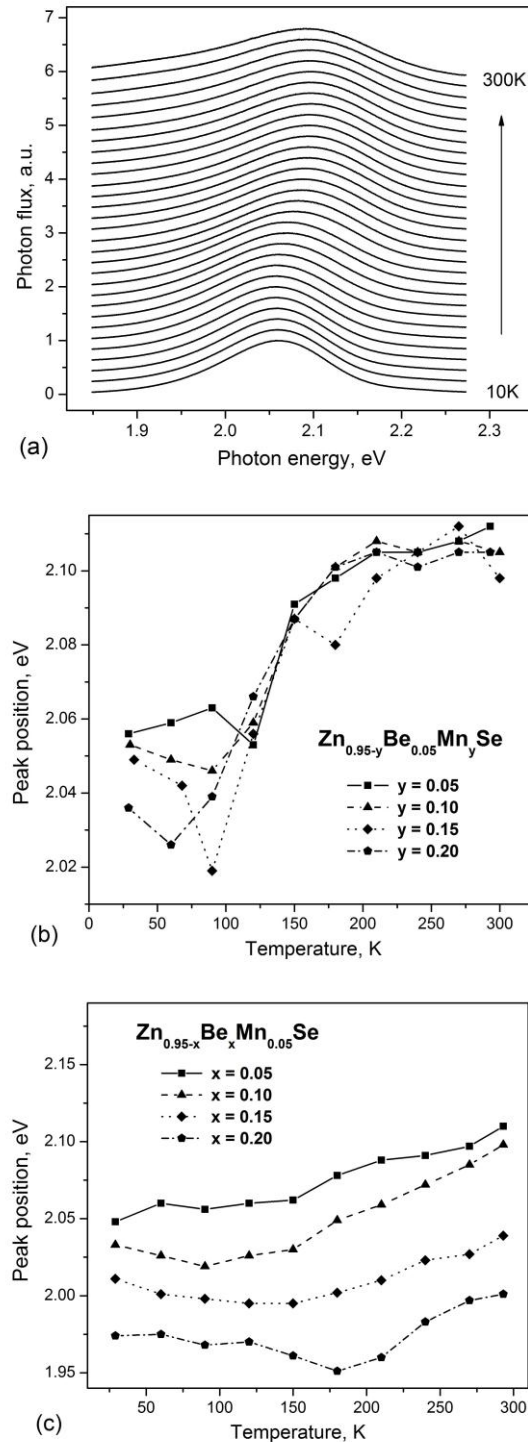
The well distinguished structure for  $\text{Zn}_{1-x-y}\text{Be}_x\text{Mn}_y\text{Se}$  with  $y=0.05$  partially disappear with increasing of Mn content probably due to broadening of particular components. This is expected effect since interactions of statistically distributed  $\text{Mn}^{2+}$  ions within the crystal increase with increasing of Mn concentration. With the increasing of Be concentration one can clearly see the revealing of higher excited levels due to increasing of the energy gap (Fig. 5b). Qualitatively similar spectra were obtained in the case of absorbance (see Fig. 4b).

Photoluminescence excitation (PLE) and absorbance spectra of  $\text{Zn}_{0.75}\text{Be}_{0.2}\text{Mn}_{0.05}\text{Se}$  crystal are presented in Fig. 6a. The very good correspondence of maxima in PLE and absorption spectra are clearly seen. Fig. 6b presents photoluminescence spectra (the low energy emission region) of  $\text{Zn}_{0.9}\text{Be}_{0.07}\text{Mn}_{0.03}\text{Se}$  crystal measured at temperatures 34 K under extrinsic excitation. The excitation energies were varied in the range from 2.3 eV to 3.1 eV as indicated in the figure. The luminescence spectra at  $T=34$  K are similar when excited separately with each of the energies: 2.32 eV, 2.48 eV, 2.67 eV, 2.88 eV and 3.08 eV. Such a behavior confirms the origin of this yellow emission as due to  $\text{Mn}^{2+}$  intra-center transition.

### 3.3 Temperature and laser power evolution of manganese emission

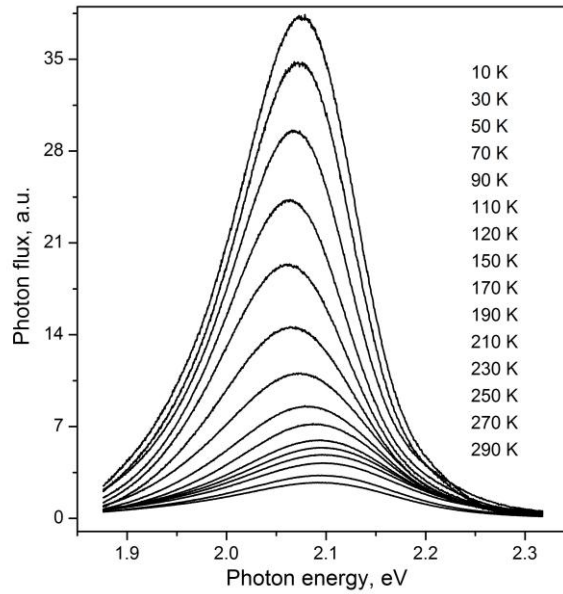
Photoluminescence spectra (the Mn-related emission region) under excitation with He-Cd laser (325 nm, 20 mW) measured at different temperatures in the range from 35 K to room temperature of  $\text{Zn}_{0.9}\text{Be}_{0.05}\text{Mn}_{0.05}\text{Se}$  crystal are presented in Fig. 7a. Figs. 7b,c show the variation of the energetic position of the maximum of this emission band versus temperature. It is clearly seen from Fig. 7b concerning  $\text{Zn}_{0.95-y}\text{Be}_{0.05}\text{Mn}_y\text{Se}$  crystals that when the temperature increases from 25 K to about 100 K the maximum of the yellow luminescence band initially shifts towards lower energies and then start to shift to opposite side (towards higher energies) with further increasing of temperature from 100 K to room temperature. Similar effect is observed for  $\text{Zn}_{0.95-x}\text{Be}_x\text{Mn}_{0.05}\text{Se}$  alloys (Fig. 7c). The only difference is, that with increasing of Be content, the temperature at which the Mn emission reach the minimum energy, shifts from about 90K for beryllium content equal 0.05 to about 180 K for  $x=0.2$ . This anomalous temperature behavior of the yellow PL band can be explained with the anomalous variation of the thermal expansion coefficient of  $\text{Zn}_{1-x-y}\text{Be}_x\text{Mn}_y\text{Se}$  with the temperature. The similar effect of manganese luminescence was observed also by other researchers for CdMnTe II-VI crystals [23]. The explanation, as the effect of negative thermal expansion of the crystal lattice with manganese ions incorporated was proposed in [24]. It was shown [23] applying crystal field theory that the main contribution to the location of manganese emission comes from the bond length in the crystal and is associated with lattice constant variation. With increasing temperature from 10K the lattice initially shrinks, causing increasing the value of the crystal field seen by Mn ion. This effect in turn influences the energetic position of the first excited state  $^4\text{T}_1(^4\text{G})$ , reducing the transition energy to the ground state  $^6\text{A}_1(^6\text{S})$ . The anomalous behavior of the manganese luminescence with the temperature was also observed in  $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$  system [25,26]. The authors explained observed effect in terms of antiferromagnetic d-d interactions of the  $\text{Mn}^{2+}$  ions, which dominate in the low temperature regime. At higher temperatures lattice expansion is the main contribution for observed blue shift of Mn emission. This explanation is consistent with the experimental observation of the shift of maximum of the Mn-related yellow emission at constant temperature towards lower

energies with increasing beryllium content in the crystals presented in Fig 1b. With increasing Be concentration in  $\text{Zn}_{0.95-x}\text{Be}_x\text{Mn}_{0.05}\text{Se}$  crystals the lattice constant decreases [27], so the lattice shrinks causing increasing the value of the crystal field seen by Mn ion. This in turn shifts the emission towards lower energies, similar to the effect caused by temperature described above.



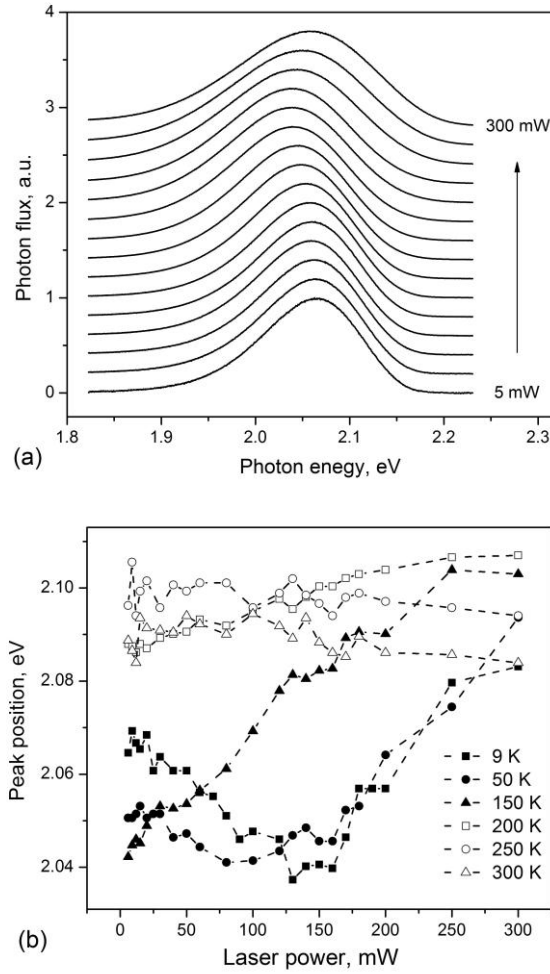
**Fig. 7** Temperature evolution of manganese photoluminescence of  $\text{Zn}_{0.9}\text{Be}_{0.05}\text{Mn}_{0.05}\text{Se}$  (a) sample. Energetic position of the maximum of Mn-related PL band as a function of temperature for  $\text{Zn}_{1-x-y}\text{Be}_x\text{Mn}_y\text{Se}$  crystals with varying content of Mn (b) and Be (c).

Fig. 8 presents temperature quenching of the manganese photoluminescence of the  $\text{Zn}_{0.9}\text{Be}_{0.05}\text{Mn}_{0.05}\text{Se}$  crystal measured under 405 nm excitation with 70 mW laser power. The entrance slit of the spectrometer and acquisition time of the camera were set to constant values 0.2 mm and 50 ms, respectively. One can see that intensity of the emission decreases from maximum at 10 K to minimum at 290 K about one order in magnitude. It is worth to notice that despite the significant decrease in intensity the Mn-ion related luminescence remains still strong and is easily visible by eye even at room temperature. This is the reason why Mn doped crystals are still attractive materials as phosphors.



**Fig. 8** Temperature quenching of the Mn luminescence of the  $\text{Zn}_{0.9}\text{Be}_{0.05}\text{Mn}_{0.05}\text{Se}$  crystal.

Another interesting behavior of the manganese emission was found for  $\text{Zn}_{1-x-y}\text{Be}_x\text{Mn}_y\text{Se}$  crystals at low temperatures under the blue (405 nm) laser excitation. The power of the laser was changed from 5 mW up to 300 mW. Since the effect was especially strong for crystals with higher manganese concentration, Fig. 9 presents results obtained for  $\text{Zn}_{0.75}\text{Be}_{0.05}\text{Mn}_{0.2}\text{Se}$  sample. One can see in picture (a) that the maximum of the manganese emission measured at 9 K shifts with the increasing laser power to the lower energies, after laser reach 150 mW the tendency is reversed. The character of the changes is temperature dependent (see Fig. 9b). Similar behavior can be found at 50 K, but for 150 K one can see monotonic tendency. At higher temperatures this effect vanishes, the maximum of the luminescence oscillate more or less around constant position.

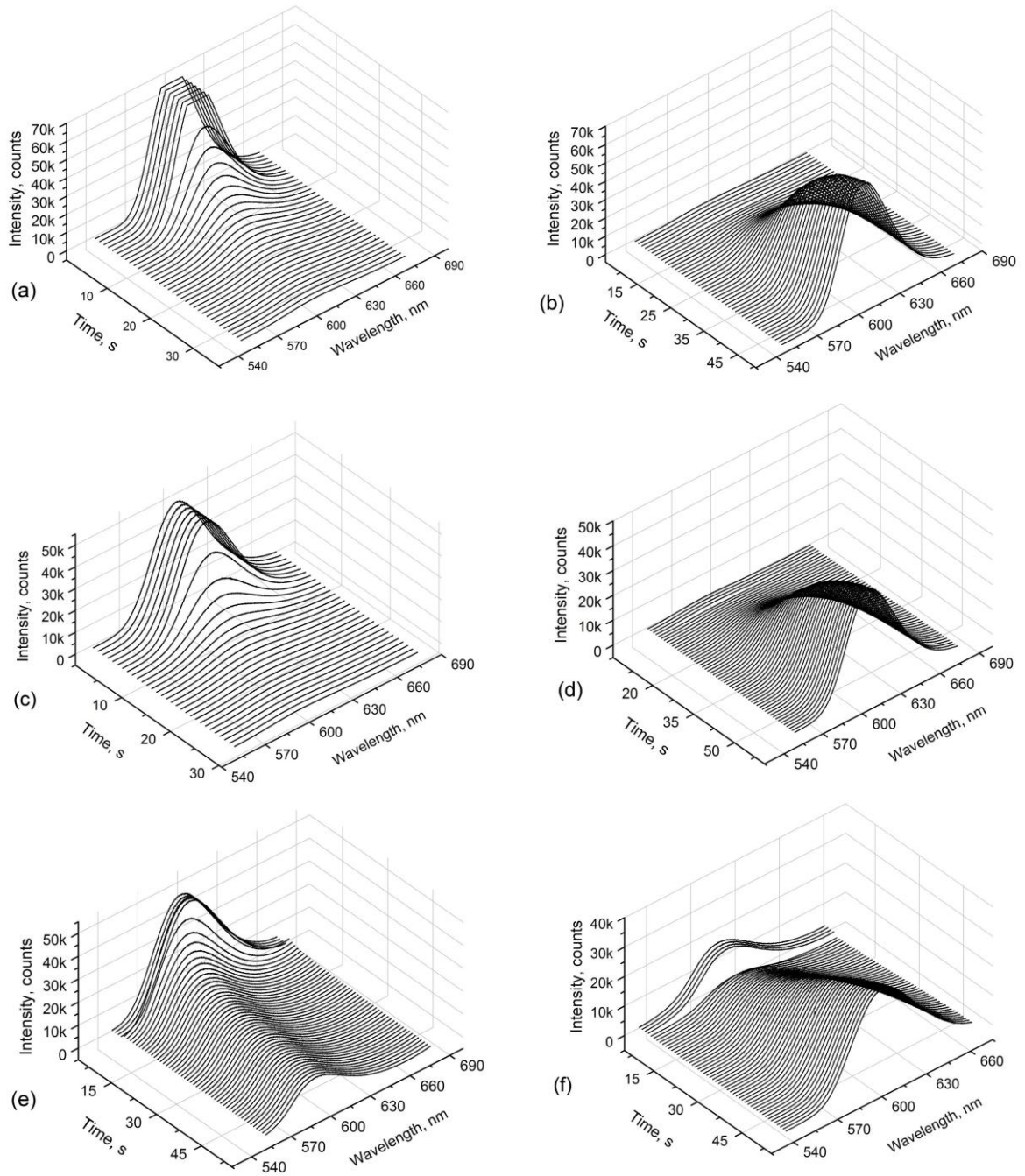


**Fig. 9** Laser power and temperature dependence of manganese photoluminescence for  $\text{Zn}_{0.75}\text{Be}_{0.05}\text{Mn}_{0.2}\text{Se}$  sample measured at 9 K (a) and for different temperatures (b).

### 3.4 Switching of manganese photoluminescence

Fig. 10 presents  $\text{Mn}^{2+}$  emission measured at three different temperatures: 10 K (a) and (b), 50 K (c) and (d), 100 K (e) and (f). During systematic investigation of the manganese luminescence with variable laser power excitation at given temperature quenching of the emission has been observed.

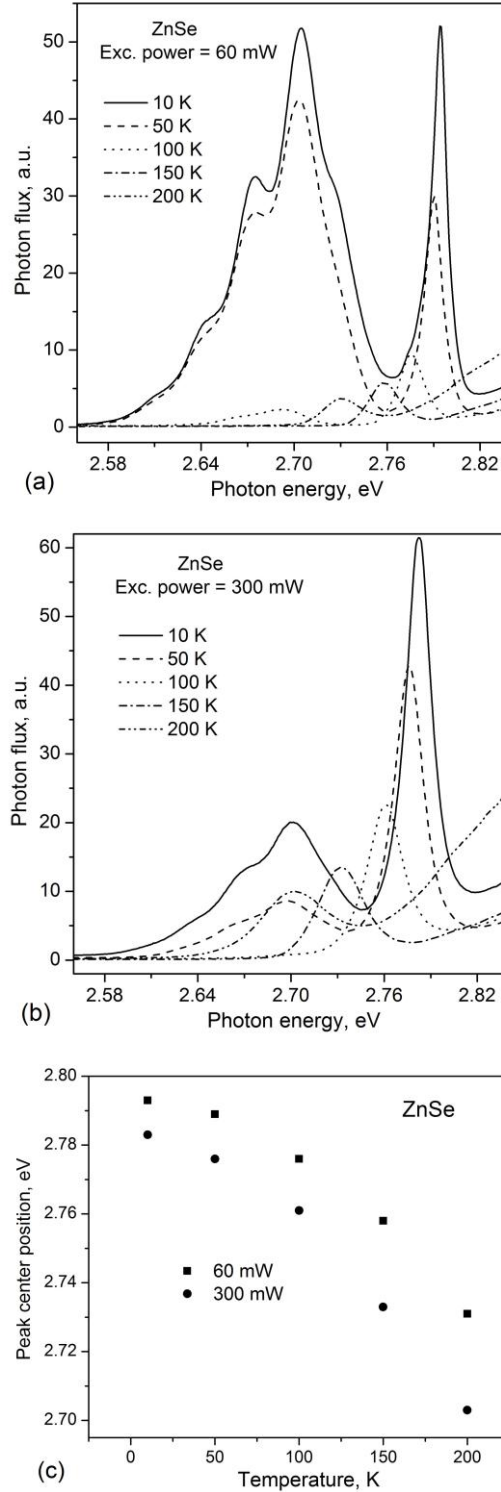
The spectra presented in pictures (a), (c) and (e) were measured in the same way. At the beginning the power of the laser was set to 70 mW and the experimental system was set to multi-acquisition mode (one spectrum per second, approximately). As one can see the signal is strong and some saturating effects can be observed in case (a). Once the system started acquisition the power of the laser has been changed to 300 mW. After tens of seconds the signal was quenched almost two orders in magnitude. Until the power of the laser is kept at maximum the signal is very weak. The pictures (b), (d) and (f) proven the effect is fully reversible. Once the power of the laser goes down to 70 mW, the intensity of the manganese luminescence is restored, again in tens of seconds.



**Fig. 10** Time-dependent manganese photoluminescence of  $\text{Zn}_{0.75}\text{Be}_{0.05}\text{Mn}_{0.2}\text{Se}$  sample measured at 10 K (a) and (b), 50 K (c) and (d) and 100 K (e) and (f) under 405 nm excitation for different laser powers.

The effect is especially strong at low temperatures, however is still present even at room temperature. Astonishing is the time scale of the observed quenching and restoring. The processes are really slow, of the order of tens of seconds. One of the explanation could be some non-radiative processes, which activate with the power of the laser.

Another phenomenon which could play the role is the heating of the sample due to high laser power. To verify how strong is the heating of the sample the photoluminescence measurements of the binary  $\text{ZnSe}$  for two excitation power (60 and 300 mW) as a function of the temperature were carried out (see Fig. 11).



**Fig. 11** Photoluminescence spectra of ZnSe crystal for 60 mW (a) and 300 mW (b) excitation power measured at several temperatures. Picture (c) presents the energy position of the exciton line in the function of temperature for both laser powers.

The binary zinc selenide was chosen because of the problem of the vicinity of the energetic position of laser radiation and exciton lines in case of the crystals investigated in this work. Since thermal properties of the ZnSe sample and mixed  $\text{Zn}_{1-x-y}\text{Be}_x\text{Mn}_y\text{Se}$  crystals are comparable, obtained results should be reliable. At the low temperature PL spectra (short-



wavelength spectral region) consist of exciton and edge luminescence. Both emission exhibit redshift with increasing temperature and are thermally quenched. Edge emission usually completely disappears at 120 K, indeed one can see in picture (a) that at 100 K edge line is still present and vanishes at 150 K. On the other hand for 300 mW excitation power one can clearly see that the edge emission is quenched at lower temperature (is visible at 50 K but vanishes at 100 K) measured in the cryostat. This observation confirms the local heating of the sample of the order of tens of kelvins, not hundreds. The same conclusion can be drawn from the change of the exciton position with increasing laser power (see Fig. 11c). For each temperature the difference in the position of excitonic line refers to the local rise of the temperature of the order of 40-50 K. Looking back at the thermal quenching of Mn-related luminescence presented in Fig. 8 one can see that its intensity decreases in the range of temperatures from 10 K to 70 K about two times. Meanwhile the intensity with the 300 mW laser power can be quenched almost two orders in magnitude. One can conclude that the heating of the sample by laser radiation is too small in order to fully explain the observed phenomenon, the exact nature of the phenomenon still remains unknown.

#### 4 Conclusions

The  $\text{Zn}_{1-x-y}\text{Be}_x\text{Mn}_y\text{Se}$  mixed crystals investigated in this work were grown by high-pressure vertical Bridgman method. The basic optical properties of  $\text{Zn}_{1-x-y}\text{Be}_x\text{Mn}_y\text{Se}$  were studied with varying temperature and excitation power. Photoluminescence spectra for samples with the lowest content of Mn and Be exhibit character typical for II-VI semiconductors with additional intensive yellow-orange manganese emission. The spectrum of the crystals grown with the highest Be and Mn content was dominated by  $\text{Mn}^{2+}$  luminescence. Evolution of the excitonic emission as the function of temperature showed monotonically red-shifted character and normal thermal broadening effect. Thanks to that energy gap of the investigated semiconductors was determined. The energy gap of the  $\text{Zn}_{0.95-y}\text{Be}_{0.05}\text{Mn}_y\text{Se}$  crystals does not vary so much with the Mn content in contrast to  $\text{Zn}_{0.95-x}\text{Be}_x\text{Mn}_{0.05}\text{Se}$  compounds, where significant increasing of the band-gap energy with increasing Be content was recorded. Obtained absorbance and photoluminescence excitation spectra allowed determining the energies of the transitions between the ground and excited states of  $\text{Mn}^{2+}$  ion. The splitting of degenerated atomic terms of  $\text{Mn}^{2+}$  ions exposed to the tetrahedral crystal field has been confirmed. Transitions from ground state to five excited states have been found and identified. Temperature and laser power dependences of Mn-related luminescence showed anomalous behavior. It turned out that the position of the  $\text{Mn}^{2+}$  luminescence do not follow monotonically variation of temperature or excitation power. Finally, switching of the manganese emission has been discovered. By applying maximum of the laser power given emission was quenched easily by two orders in magnitude. The effect was especially strong at low temperature and for crystals with high manganese content, however was observed also at room temperature and for the lowest manganese concentration. It turned out that the phenomenon is long on the time scale, it is caused by the intensity of exciting laser radiation and it is reversible. It was shown that the heating of the sample by laser radiation is too small in order to fully explain the observed phenomenon; the exact nature of the phenomenon still remains unknown.



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